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B H BARETZ ET AL. JUN 84 N00014-82-C-0202

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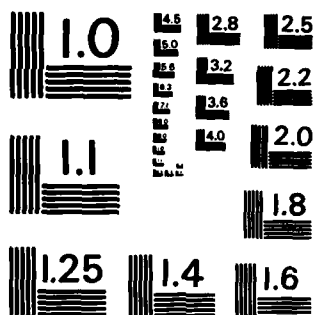
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**FINAL TECHNICAL REPORT  
TO THE  
OFFICE OF NAVAL RESEARCH**

AD-A148 460

**INVESTIGATION OF  
CHEMILUMINESCENT SYSTEMS**

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AN INVESTIGATION OF  
CHEMILUMINESCENT REACTIONS

FINAL

SUMMARY TECHNICAL REPORT

TO

THE OFFICE OF NAVAL RESEARCH

CONTRACT NO. N00014-82-C-0202

BY: B. H. BARETZ; W. J. TRZASKOS, L. ELLIOTT  
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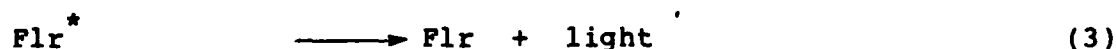
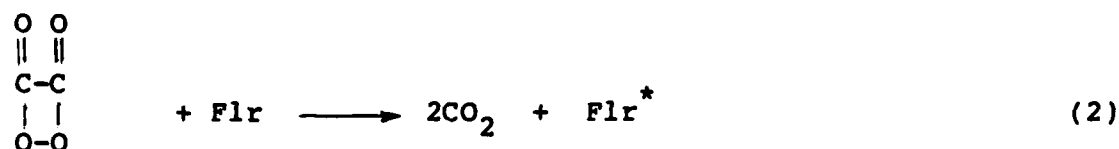
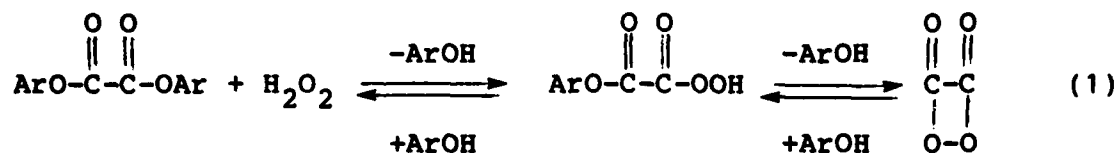
### Abstract

The utilization of aqueous environments as media for peroxyoxalate chemiluminescence of rubrenesulfonate was further explored. The fluorescence and chemiluminescence of rubrenesulfonate was found to increase with the addition of Deceresol NI, a nonionic surfactant, and polyvinylpyrrolidone (PVP), a nonionic water-soluble polymer. Although the chemiluminescence of rubrenesulfonate was found to be enhanced in the presence of sodium decylsulfate (SDeS), no enhancement was observed for its fluorescence. However, in the presence of hexadecyltrimethylammonium chloride (HDTCl), the fluorescence of rubrenesulfonate was enhanced, while no influence on its peroxyoxalate chemiluminescence was observed. The greatest chemiluminescence enhancement was noted with formulations that contained both PVP and SDeS, revealing a dramatic synergistic effect of surfactants with polymers on aqueous peroxyoxalate chemiluminescence. The peroxyoxalate chemiluminescence enhancements observed with Deceresol NI and SDeS were due to micellar effects. The enhancements observed with the PVP/SDeS formulation suggested the involvement of polymer:surfactant aggregates in the chemiluminescence reaction. The PVP/SDeS formulation provided for a 270% increase in chemiluminescence over that obtained with Deceresol NI.

## INTRODUCTION

It has been more than twenty years since research in chemical illuminating systems was initiated at the American Cyanamid Company.<sup>1</sup> After some initial exploratory reports,<sup>2</sup> the Cyanamid research program rapidly focussed on the use of oxalic esters as reactants in a "chemical light" system.<sup>3</sup> The culmination of this initial research program<sup>4</sup> led to, after some time, the development of a practical, portable chemical light formulation which is in current commercial and governmental use for a wide variety of applications.

Despite the passage of time since its initial discovery, and the considerable interest of the scientific community,<sup>5</sup> the chemistry associated with oxalic ester chemiluminescence remains somewhat of a mystery. This system is called "peroxyoxalate chemiluminescence,"<sup>6</sup> (a name we embrace within for descriptive purposes), since hydroperoxyoxalate monoesters are "presumed" reaction products of the initial chemical event (equation 1). Eventually, an "energy-releasing intermediate" is thought to be formed (equation 2), a "dioxetanedione"<sup>7</sup> which, in the presence of a fluorescer, reacts to cause light emission and carbon dioxide production (equation 3).<sup>7</sup> This vague descriptive mechanism (equation 1-3) provides a useful mechanistic hypothesis to discuss peroxyoxalate chemiluminescence, despite the absence of hard evidence to document its viability.



Even with the extensive scientific interest and research in chemiluminescence over the past decade, peroxyoxalate chemiluminescence remains as one of the most efficient man-made chemical light systems. Nevertheless, we are interested in studying other formulations of the peroxyoxalate chemiluminescence system. From the working hypothesis presented above (equation 1-3), it is clear that the chemiluminescence reaction efficiency  $\Phi_{\text{CL}}$ , can be separated into the efficiency for production of the energy releasing intermediate,  $\phi_{\text{eri}}$ ; the efficiency of fluorescer excited state production,  $\phi_{\text{r}}$ ; and the quantum yield for fluorescence,  $\Phi_{\text{f}}$  (equation 4).

$$\Phi_{\text{CL}} = \phi_{\text{eri}} \phi_{\text{r}} \Phi_{\text{f}} \quad (4)$$

The best chemiluminescence quantum yield reported for a peroxyoxalate system is of the order of 0.35.<sup>8</sup> Since the fluorester (1-chloro-9,10-bisphenylethynylantracene, ClBPEA) utilized in that system has a fluorescence quantum yield of nearly unity,<sup>9</sup> the chemiluminescence inefficiencies are typically thought to reflect inefficient chemiexcitation of the fluorester (i.e.;  $\phi_{\text{eri}}$  and  $\phi_{\text{r}} \ll 1.0$ ). However, we note that either the oxalic esters, or phenolic byproducts, have been known to quench the fluorescence of ClBPEA.

The explosion of interest in utilizing aqueous organized assemblies as environments for modifying the photophysical and photochemical pathways of a multitude of excited state processes has spurred interest in applications in the area of aqueous chemiluminescence. Preliminary studies have supported the viability of modifying peroxyoxalate chemiluminescence to a water-based system.<sup>10</sup> Our expectation has been that an appropriate formulation could overcome some of the observed inefficiencies in the organic based system. Certainly, sequestering of reactants and products from fluorester, a goal with precedence in aqueous organized assemblies, could diminish the quenching of luminescence observed in the organic based systems. In addition the inefficiencies associated with chemiexcitation,  $\phi_{\text{r}}$ , may be overcome with the modification of dynamics associated with reaction pathways typically observed within organized assemblies. The promise of chemiluminescence enhancements in these media is discussed in this report of our work on peroxyoxalate chemiluminescence in aqueous environments.



## EXPERIMENTAL

Preparation of N-(2-morpholinoethyl)trifluoromethane sulfonamide.<sup>10</sup> Trifluoromethanesulfonic anhydride (100 g; 0.354 mole) was added dropwise to a stirred solution of N-(2-aminoethyl)morpholine (92.3 g; 0.709 mole) in methylene chloride (600ml) at 0°C under an argon atmosphere. After complete addition the reaction mixture was stirred for 4 hours under argon. The white precipitate was then filtered off and the filtrate concentrated. The resulting crude product was recrystallized from cyclohexane yielding the desired product (81.3 g; 88% yield): mp 107-109°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 5.75 (s, 1H), 3.75 (m, 4H), 3.3 (+, 2H, 2.5 (m, 6H); IR (CH<sub>2</sub>Cl<sub>2</sub>) 3300, 1360, and 1200 cm<sup>-1</sup>.

Preparation of N,N'-Bis(2-morpholinoethyl)-N,N'-bis(trifluoromethyl sulfonyl)oxamide (METO).<sup>10</sup> Oxalyl chloride (25ml; 0.286 mole) was added dropwise to a stirred solution of N-(2-morpholinoethyl)trifluoromethane sulfonamide (150 g; 0.573 mole) and triethylamine (80ml; 0.573 mole) in freshly distilled THF (1500ml) at 0°C, under an argon atmosphere. The rate of addition was very slow in order to maintain a reaction temperature of 0°C. After complete addition the reaction mixture was stirred for 16 hours under argon. The white precipitate was then filtered off and the filtrate was concentrated. The resulting viscous oil was poured into 750ml of rapidly stirred petroleum ether which caused the product to precipitate yielding 158.6 grams (98% yield): mp

68-70°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 3.75 (m, 6H), 2.5 (m, 6H); IR ( $\text{CH}_2\text{Cl}_2$ ) 2950, 1740, 1720, 1370 and  $1200\text{ cm}^{-1}$ .

4,4'-Oxalyl-bis[(trifluoromethylsulfonyl)imino]ethylene-bis-(N-methylmorpholinium)trifluoromethane sulfonate (METO).<sup>10</sup> Methyl trifluoromethanesulfonate (65ml; 0.574 mole) was added dropwise to a stirred solution of METO (125 g; 0.216 mole) in dry methylene chloride (1000ml) at 0°C, under argon. After complete addition the reaction mixture was stirred for 16 hours under argon. The resulting precipitate was suction filtered and washed with methylene chloride. The product was dried overnight under vacuum yielding 188.0 grams (96% yield): mp 165-168°C;  $^1\text{H}$  NMR ( $\text{DMSO } d_6$ ) 3.9 (m, 4H), 3.7 (m, 4H), 3.5 (m, 4H), 3.2 (s, 3H; IR (nujol and halocarbon oil) 2950, 1745, 1728, 1425, and  $1200\text{ cm}^{-1}$ .

1,1,3-Triphenylpropargyl Alcohol.<sup>11</sup> n-Butyllithium (45.0 g; 0.70 mole) was added dropwise to a stirred solution of phenylacetylene (70.0 g; 0.69 mole) in dry THF (625ml) at 0°C, under an argon atmosphere. After complete addition the reaction mixture was stirred for 30 minutes. Benzophenone (125.0gr; 0.69 mole) in THF (500ml) was then added dropwise at room temperature. After complete addition the reaction mixture was stirred for 16 hours. Ammonium chloride (saturated, 3L) was then added slowly to the reaction mixture. The resulting reaction mixture was extracted with diethyl ether (3x1L). The ether layers were combined, washed with water (2x1L) and then a saturated NaCl solution (1x1L), separated, and dried using magnesium sulfate. The ether

solution was concentrated yielding a yellow oil. The crude product was poured into hexanes (750ml) causing the product to precipitate. The precipitate was suction filtered and then dried overnight under vacuum, yielding 157.8 grams of product (80% yield): mp 79-80°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 7.8 (m), 7.3 (m), 2.9 (s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) ppm 91.7, 87.3, and 74.9; IR ( $\text{CH}_2\text{Cl}_2$ ) 3600, 3050, and 2260  $\text{cm}^{-1}$ .

1,1,3-Triphenylpropargyl Chloride. Thionyl chloride (4.0ml; 55 mmole) in methylene chloride (20ml) was added dropwise to a stirred solution of 1,1,3-triphenylpropargyl alcohol, in methylene chloride (100ml), at -5°C, under an argon atmosphere. After complete addition, the reaction mixture was stirred for 1 hour at 0°C and 1 hour at room temperature. After that time an IR spectrum was taken, which confirmed that all of the alcohol had reacted. The reaction mixture was then concentrated yielding a light brown oil (14.5 g). This product was used without further purification.

Rubrenesulfonate. 1,1,3-Triphenylpropargyl chloride (14.5 g; 47.9 mmole) was dissolved in 15ml of xylene and 4ml of quinoline and heated to reflux in the dark under an argon atmosphere for 16 hours. After that time the reaction mixture was allowed to cool. The resulting precipitate was suction filtered. The precipitate was dissolved in methylene chloride (200ml) and washed one time each with  $\text{NaHCO}_3$  (aq),  $\text{HCl}$  (aq),  $\text{H}_2\text{O}$  and  $\text{NaCl}$  (aq). The methylene chloride was separated, dried with sodium sulfate, and

concentrated, yielding 6.2 grams of rubrene.

Fuming sulfuric acid (18%  $\text{SO}_3$ , 25ml) was added dropwise to a stirred solution of rubrene (5.0 g) in a mixture of ethylene dichloride (300ml), dioxane (300ml), and methylene chloride (150ml) at room temperature. After complete addition the reaction mixture was stirred for 16 hours. Aqueous sodium carbonate was then added slowly to the reaction mixture until the pH was seven. The aqueous phase was then separated and washed with methylene chloride. The aqueous phase was concentrated leaving the crude product. This crude product was dissolved in methanol (500ml) and filtered. The methanol solution was concentrated yielding 4.6 grams of product. Analysis by FAB mass spectrometry confirmed the product was a mixture of 90% mono-sulfonate and 10% disulfonate.

Fluorescence Studies. All fluorescence spectra were obtained from a Perkin-Elmer MPF-44E spectrofluorimeter. The spectrofluorimeter was interfaced with a Bascom-Turner model 4120 recorder, which graphically recorded and digitized all data. Each sample was excited at 470 nm, and the emission spectrum recorded from 500 nm to 700 nm.

The Influence of Non-Ionic Detergent on Fluorescence Yields.

The fluorescence spectrum of a  $1.0 \times 10^{-5}\text{M}$  aqueous rubrenesulfonate solution was recorded. Samples of  $1.0 \times 10^{-5}\text{M}$

rubrenesulfonate solution were prepared which contained increasing concentrations of Deceresol NI from  $28 \times 10^{-6} \text{M}$  to  $1.1 \times 10^{-3} \text{M}$ . The fluorescence emission spectrum was recorded for each increase in surfactant concentration, relative to the surfactant-free solution. The relative intensity was plotted as a function of increasing surfactant concentration.

Fluorescence of Rubrenesulfonate in the Presence of Polyvinylpyrrolidone. The fluorescence spectrum of a  $1.0 \times 10^{-5} \text{M}$  aqueous rubrenesulfonate solution was recorded. Subsequently, solutions were prepared which contained rubrenesulfonate and increasing polyvinylpyrrolidone concentrations from 0.01% to 0.50% (w/v). The fluorescence emission spectrum was recorded for each increase in polymer concentration, relative to the polymer-free aqueous solution.

Fluorescence of Rubrenesulfonate in Protic Solvents. The fluorescence spectrum was recorded for a  $1.0 \times 10^{-7} \text{M}$  rubrenesulfonate solution in water. From a stock solution of  $1.0 \times 10^{-4} \text{M}$  rubrenesulfonate in water,  $1.0 \times 10^{-7} \text{M}$  solutions were prepared in solvents of decreasing polarity: methanol, ethanol and n-propanol. The fluorescence emission spectrum was recorded for each sample, relative to rubrenesulfonate in water.

Chemiluminescence Studies. All chemiluminescence intensity studies were performed using a chemiluminometer.<sup>7</sup> The chemiluminometer was interfaced with the Bascom-Turner model 4120

recorder, which graphically recorded and digitized all data. Each sample contained the following standard formulation: METQ, 0.063 g; rubrenesulfonate, 0.01 g; sodium perborate tetrahydrate, 0.23 g, and 2.5ml water. It is important to note that all chemiluminescence intensity curves are recorded immediately after the addition of water, at an emission wavelength of 575 nm.

Effect of Non-Ionic Surfactant on Rubrenesulfonate Chemiluminescence. The chemiluminescence intensity curve was recorded for the standard formulation. Solutions of increasing Deceresol NI concentrations from  $1.0 \times 10^{-5} \text{ M}$  to  $3.0 \times 10^{-3} \text{ M}$  were prepared and added to the standard formulation. The chemiluminescence intensity curves were recorded for each increase in concentration, relative to the standard formulation. The relative chemiluminescence intensity was plotted as a function of increasing surfactant concentration.

Effect of Water-Soluble Polymers on Rubrenesulfonate Chemiluminescence. The chemiluminescence intensity curve was recorded for the standard formulation. Several standard formulations were prepared, to which increasing polyvinylpyrrolidone concentrations, from 0.01% to 1.0% (w/v), were added. The chemiluminescence intensity curves were recorded for each concentration, relative to the standard formulation.

Effect of Anionic Surfactant on Rubrenesulfonate Chemiluminescence. The chemiluminescence intensity curve was

recorded for the standard formulation. Increasing sodium decyl sulfate concentrations from  $1.0 \times 10^{-4}M$  to  $4.0 \times 10^{-2}M$  were added to standard formulation. The chemiluminescence intensity curves were recorded, relative to the standard formulation. The relative chemiluminescence intensity was plotted as a function of increasing surfactant concentration.

Effect of Chain Length on Surfactant Chemiluminescence Enhancement. The chemiluminescence intensity curve was recorded for the standard formulation. Subsequent chemiluminescence intensity curves were recorded for standard formulations which contained 1% (w/v) concentrations of sodium alkylsulfate surfactants of varying carbon chain lengths. Each curve obtained was recorded relative to that obtained for the standard formulation.

Effect of Chain Length on Polymeric Chemiluminescence Enhancement

The chemiluminescence intensity curve was recorded for a standard formulation which contained 1% (w/v) polyvinylpyrrolidone (PVP). Additional standard formulations were prepared which contained 1% (w/v) PVP and 1% (w/v) of a sodium alkylsulfate of increasing carbon chain length. The chemiluminescence intensity curve was recorded for each sample, relative to the curve obtained from the standard formulation containing 1% PVP.

Maximum Chemiluminescence Intensity from Several Different Additives. The chemiluminescence intensity curve was recorded for the standard formulation. Four additional standard formulations were prepared, and to each was added the following amount of polymers or surfactant: 1% (w/v) PVP;  $2.0 \times 10^{-3}$  M Deceresol NI;  $3.0 \times 10^{-2}$  M sodium decyl sulfate; and 1% (w/v) PVP and  $3.0 \times 10^{-2}$  M sodium decyl sulfate. The chemiluminescence intensity curve was recorded for each of the above solutions, relative to the standard formulation.



## RESULTS

### Fluorescence - The Presence of Surfactants-Hydrophobic Effects

In the presence of protic solvents, the fluorescence of rubrenesulfonate increases as a function of hydrophobicity (Figure 1). For example, stepwise increases are observed in the fluorescence intensity as the aqueous solvent is replaced with methanol, ethanol, or n-propanol. Paralleling the effect of hydrophobicity, the fluorescence of rubrenesulfonate, in water, increases with the addition of Deceresol NI. For Deceresol NI concentrations less than  $1 \times 10^{-5}M$ , no fluorescence enhancement is observed. However, at higher concentrations the fluorescence enhancement gradually increases. At concentrations of Deceresol greater than the critical micelle concentration (cmc),<sup>12</sup> the enhancement levels off (Figure 2).

In contrast to the effects observed with the nonionic Deceresol, no fluorescence enhancement was observed with the aqueous solubilization of rubrenesulfonate in the presence of sodium decylsulfate, an anionic surfactant. This lack of an increase in fluorescence intensity was observed even at concentrations greater than the surfactant cmc. However, a substantial enhancement, similar to that observed with n-propanol, was observed with solubilization of rubrenesulfonate in hexadecyltrimethylammonium chloride micelles.

Figure 1. Fluorescence Emission as a Function of  $\epsilon$ , Solvent Polarity. Rubrenesulfonate solutions ( $1 \times 10^{-7}$  M) were excited at 470 nm.

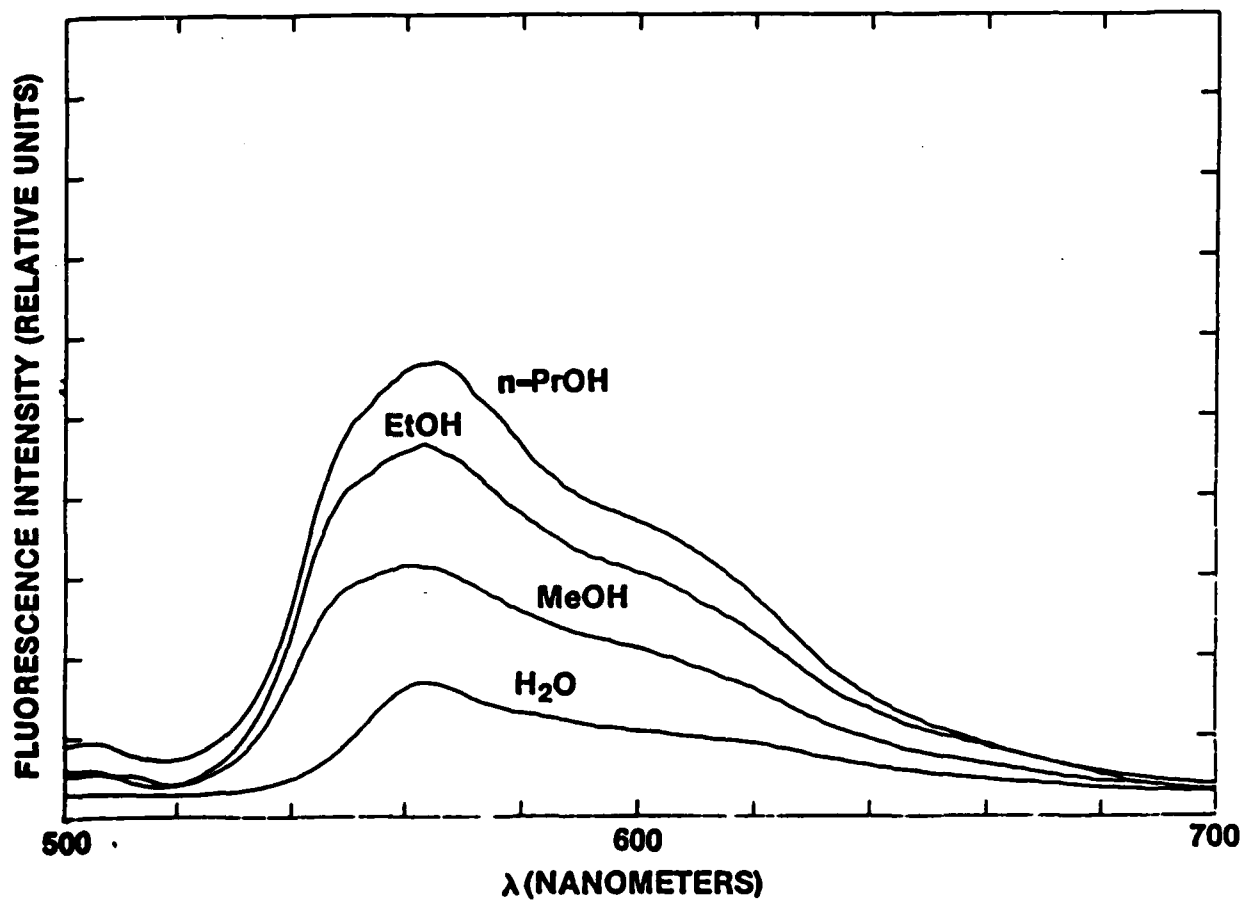
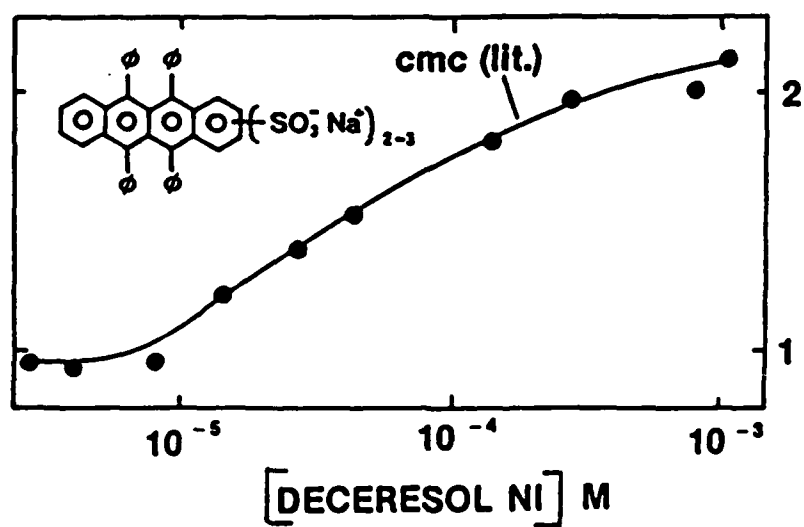
**FLUORESCENCE OF RUBRENESULFONATE IN PROTIC SOLVENTS**

Figure 2. Fluorescence Emission as a Function of Deceresol  
NI Concentration. Aqueous rubrenesulfonate solutions ( $1 \times 10^{-5}$  M) were excited at 470 nm.

**FLUORESCENCE INTENSITY**



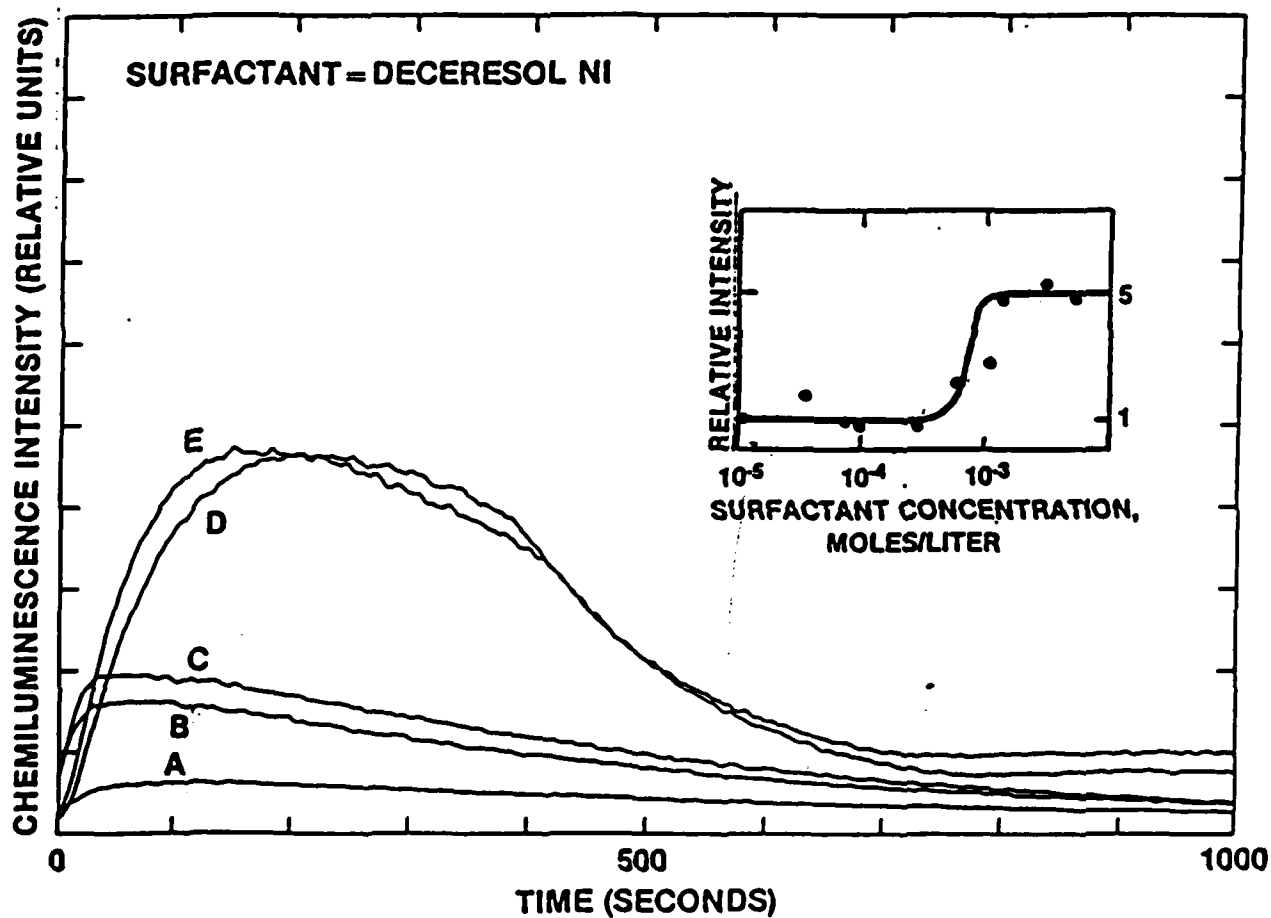
### Chemiluminescence - The Role of Surfactants

There have been two previous reports describing conditions for peroxyoxalate chemiluminescence using METQ and rubrenesulfonate as integral components in the formulation. The pioneering work, reported by Mohan, et.al.,<sup>10</sup> describes the aqueous peroxyoxalate chemiluminescence yields when the nonionic surfactant Deceresol NI is present in the formulation (at  $1 \times 10^{-3}M$ ). The reported quantum yield is 0.0476 einsteins/mole.<sup>10</sup> The second report qualitatively describes the emission observed with METQ and rubrenesulfonate, in the presence of  $4 \times 10^{-2}M$  Deceresol NI, as "intense yellow-red light....(that) lasts for 10-20 minutes."<sup>13</sup>

Deceresol NI is a commercial polyethoxylated nonylphenol. At the concentration utilized in the previous two studies, the aqueous solutions of Deceresol NI should contain micelles.<sup>12</sup> Hence, the observed increase in peroxyoxalate chemiluminescence may represent a manifestation of micellization. This hypothesis has been supported by the observation that the chemiluminescence intensity increases with Deceresol NI concentration (Figure 3) in a manner that suggests the increase results from surfactant aggregation. The maximal increase in chemiluminescence, at a Deceresol NI concentration of  $1 \times 10^{-3}M$ , is 5-fold, similar to that observed in the previous work.<sup>10</sup> The rapid increase in chemiluminescence intensity occurs at around  $6 \times 10^{-4}M$ .

Figure 3. Aqueous Peroxyoxalate Chemiluminescence of Rubrenesulfonate in the Presence of Deceresol NI. The chemiluminescence emission, monitored at 575 nm, was initiated by the addition of water. The Deceresol NI concentrations ranged from  $1 \times 10^{-5}$  M to  $3 \times 10^{-3}$  M.

# EFFECT OF NONIONIC SURFACTANT ON RUBRENESULFONATE CHEMILUMINESCENCE

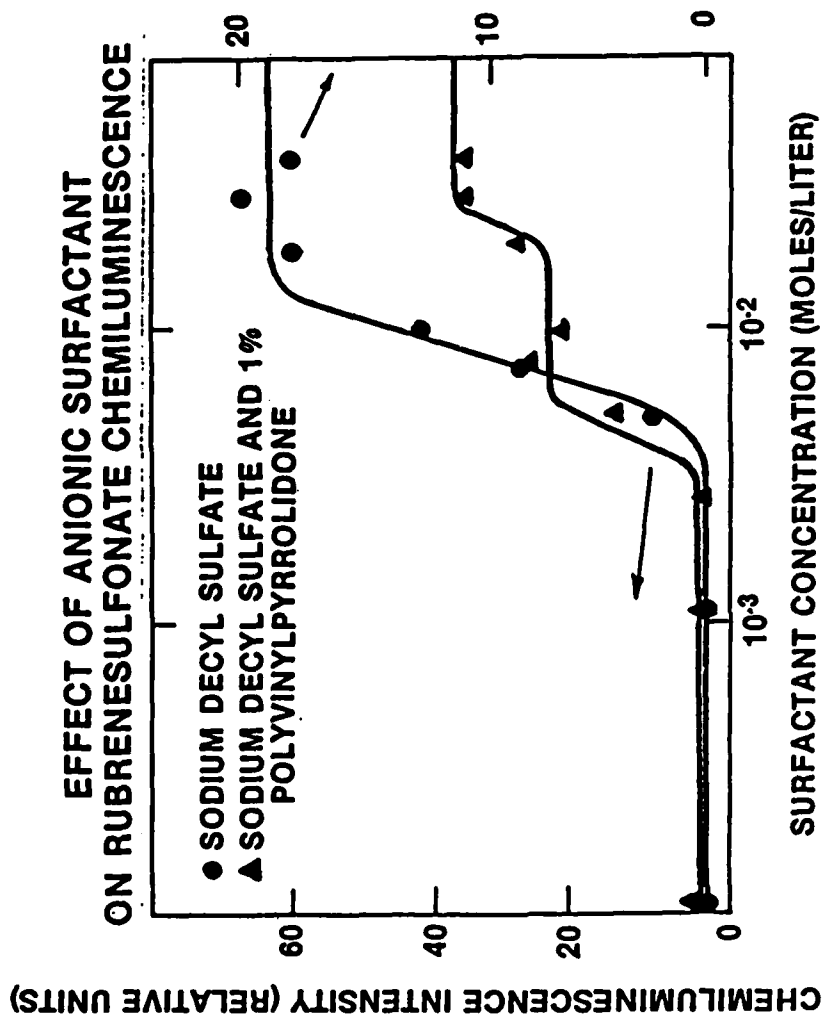




It is clear, from equation 4, that the chemiluminescence quantum yield can never be greater than the quantum yield of emission from the fluorescer, in that particular environment. Although it is tempting to explore peroxyoxalate chemiluminescence in those aqueous environments that increase the fluorescer's emission intensity, it is important to consider that peroxyoxalate chemiluminescence and fluorescence quantum yields, for a particular fluorescer and formulation, need not move in tandem. With this in mind, the effects of sodium alkylsulfates on peroxyoxalate chemiluminescence were examined despite the fact that these anionic surfactants had little influence on rubrenesulfonate's fluorescence quantum yields.

The peroxyoxalate chemiluminescence quantum yields were shown to be dramatically influenced by the introduction of sodium decylsulfate (SDeS) to the aqueous formulation (Figure 4). For SDeS concentrations less than  $3 \times 10^{-3}M$ , the surfactant played little role in influencing the chemiluminescence. However, with SDeS concentrations greater than  $2 \times 10^{-2}M$ , a dramatic increase in peroxyoxalate chemiluminescence was observed. Although a rather broad transition is evident in Figure 4, the dramatic increase in chemiluminescence seems to begin around the "cmc" of SDeS.

Figure 4. Aqueous Peroxyoxalate Chemiluminescence of Rubrenesulfonate in the Presence of Sodium Decylsulfate (SDeS). The chemiluminescence emission, monitored at 575 nm, was initiated by the addition of water. The SDeS concentrations ranged from  $1 \times 10^{-4}$  M to  $4 \times 10^{-2}$  M. The polyvinylpyrrolidone (m.w. 40,000) concentration was 1% w/v.



Similarly the effect of varying chain length, in the sodium alkylsulfate series, on the fluorescence and peroxyoxalate chemiluminescence yields of rubrenesulfonate was explored. Not surprisingly, the  $C_6$ ,  $C_7$ ,  $C_8$ , and  $C_{12}$  sodium alkylsulfates had little influence on the fluorescence of rubrenesulfonate - paralleling the observations with SDeS. However, the  $C_{12}$  analog, sodium dodecylsulfate (SDS) does increase the peroxyoxalate chemiluminescence of rubrenesulfonate (Figure 5), although less dramatically than that observed with the  $C_{10}$  - analog, SDeS.

#### Chemiluminescence - The Role of Polyvinylpyrrolidone

Organic sulfonates are known to effectively associate with polyvinylpyrrolidone dissolved in aqueous solution.<sup>14</sup> In many examples, the association exposes the water soluble sulfonate to a hydrophobic environment generated by the hydrocarbon backbone of the polyvinylpyrrolidone. Unlike the sodium alkylsulfates, polyvinylpyrrolidone was instrumental in increasing the fluorescence intensity of aqueous solubilized rubrenesulfonate (Figure 6) approximately 2-fold. The peroxyoxalate chemiluminescences of rubrenesulfonate was similarly increased, in the presence of polyvinylpyrrolidone (Figure 7), although less so than the enhancement observed with SDeS.

Figure 5. Aqueous Peroxyoxalate Chemiluminescence of Rubrenesulfonate in the Presence of Sodium Alkylsulfates. The chemiluminescence emission, monitored at 575 nm, was initiated by the addition of water. The surfactant concentration, in each case, was 1% w/v.

# EFFECT OF CHAIN LENGTH ON SURFACTANT CHEMILUMINESCENCE ENHANCEMENT

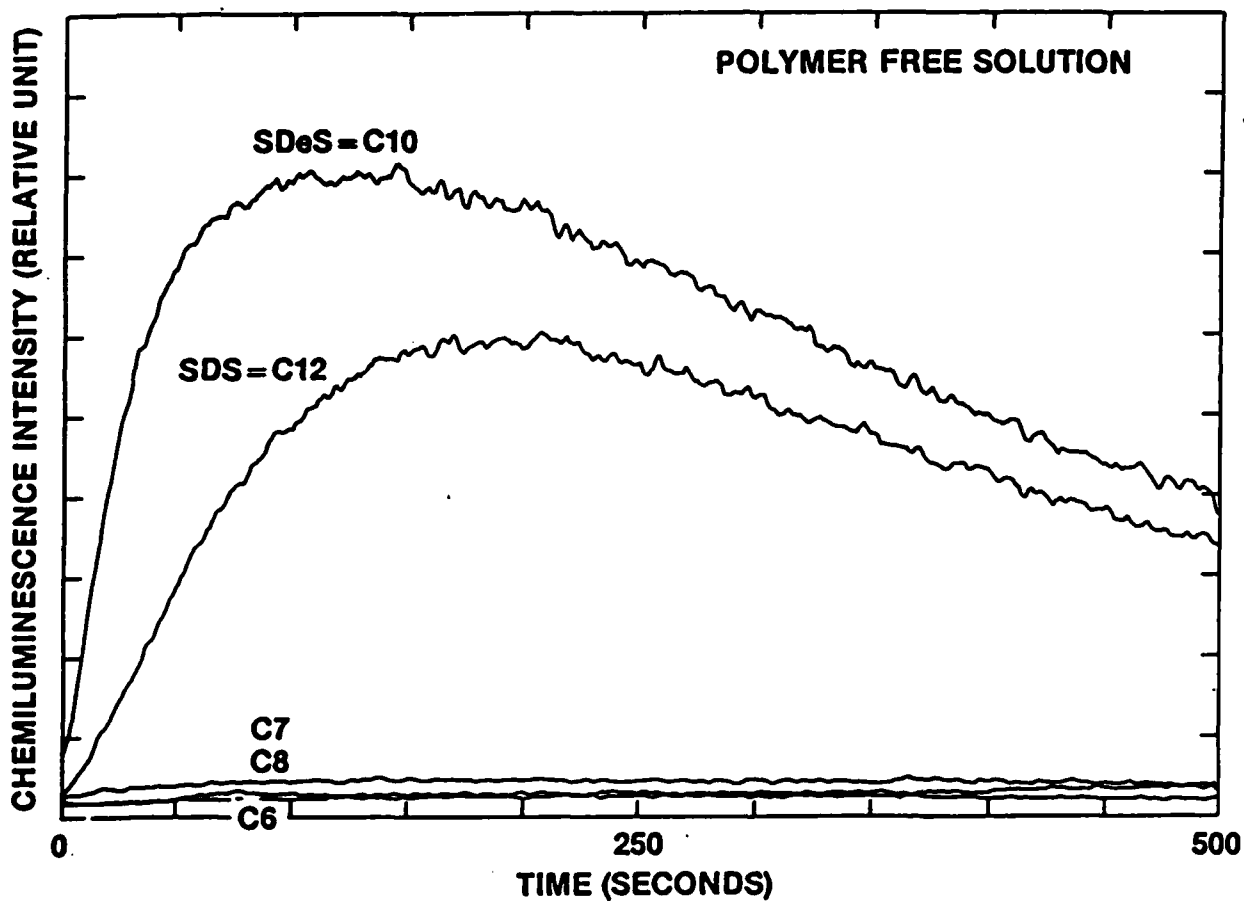


Figure 6. Fluorescence of Rubrenesulfonate in the Presence of Polyvinylpyrrolidone<sub>5</sub>. The aqueous solutions of rubrenesulfonate ( $1 \times 10^{-5}$  M) were excited at 470 nm.

FLUORESCENCE OF RUBRENESULFONATE  
IN THE PRESENCE OF POLYVINYLPYRROLIDONE.

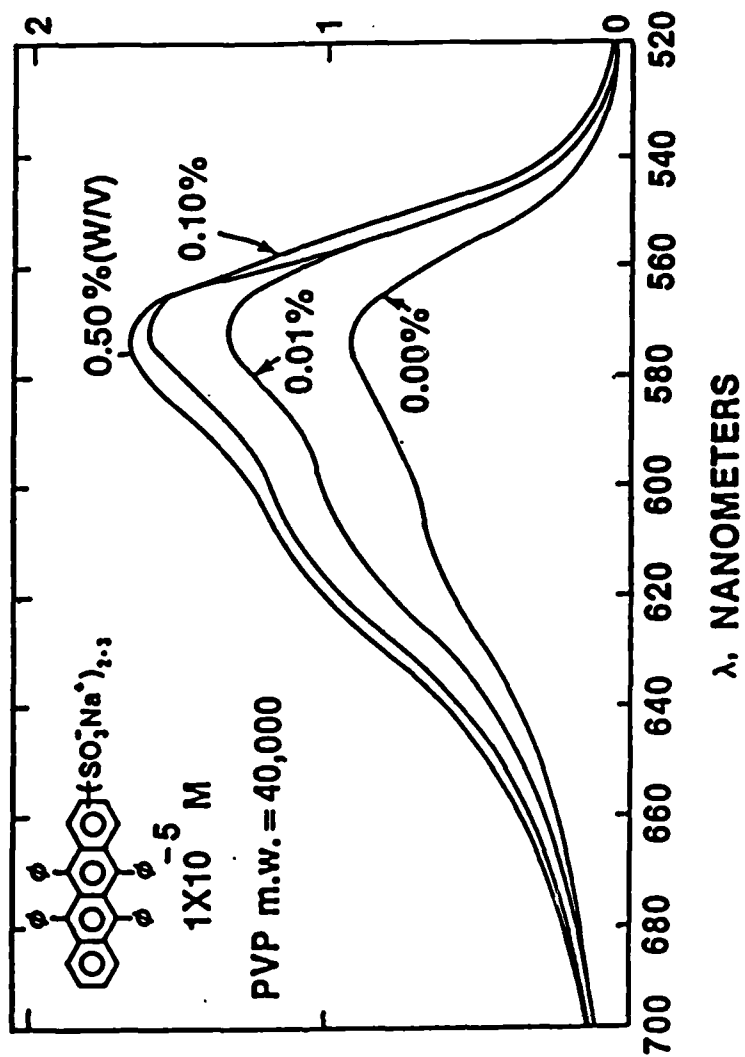


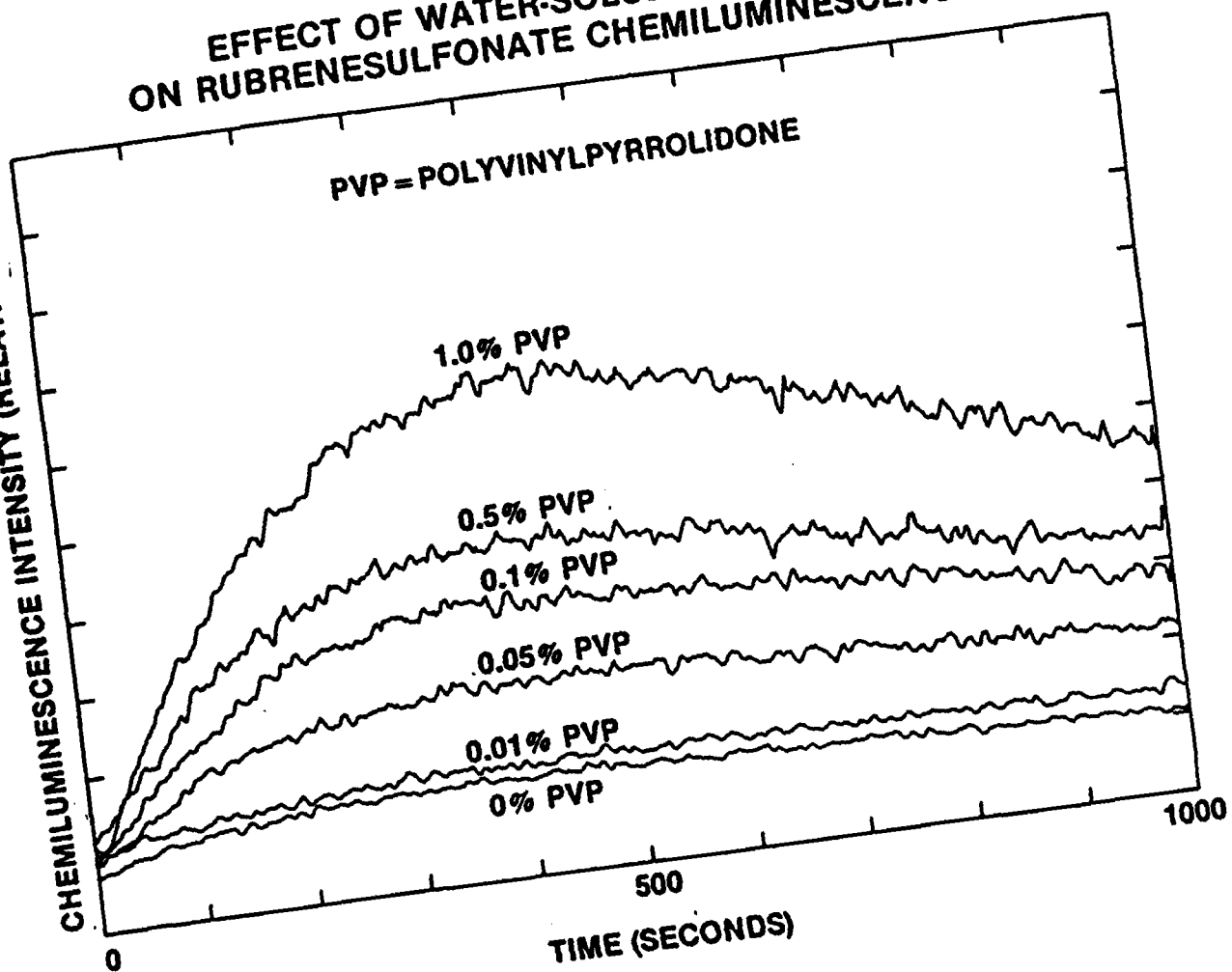


Figure 7. Aqueous Peroxyoxalate Chemiluminescence of Rubrenesulfonate in the Presence of Polyvinylpyrrolidone. The chemiluminescence emission, monitored at 575 nm, was initiated by the addition of water. The PVP (m.w. 40,000) concentrations ranged from 0.0 to 1.0% w/v.

# EFFECT OF WATER-SOLUBLE POLYMER ON RUBRENESULFONATE CHEMILUMINESCENCE

PVP = POLYVINYLPIRROLIDONE

CHEMILUMINESCENCE INTENSITY (RELATIVE UNITS)



Chemiluminescence - Cooperative Effects of Sulfate Surfactants  
with Polyvinylpyrrolidone

The anionic surfactants, sodium alkylsulfates, are known to associate with polyvinylpyrrolidone dissolved in aqueous solution.<sup>15</sup> Since the peroxyoxalate chemiluminescence and fluorescence of rubrenesulfonate increased in the presence of polyvinylpyrrolidone, the influence of sodium alkylsulfate in the polymer formulation was next examined.

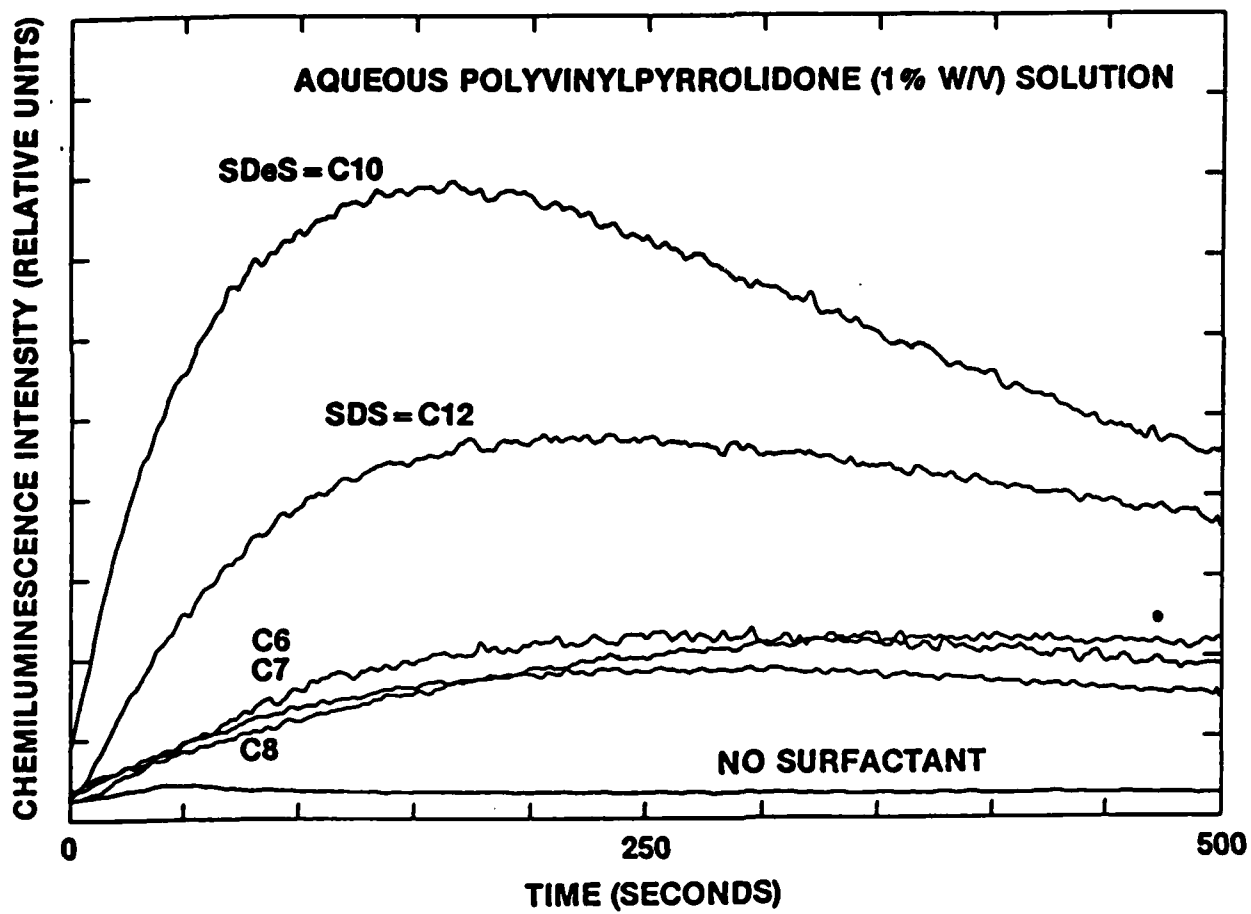
In fact, as SDeS is added to the polymer formulation of rubrenesulfonate, the fluorescence intensity decreases. However, with respect to the peroxyoxalate chemiluminescence of rubrenesulfonate, the luminescence intensity dramatically increases with addition of sodium decylsulfate (Figure 4). The maximal increase in chemiluminescence intensity, occurs with surfactant concentrations greater than  $3 \times 10^{-2} \text{M}$ .

It is important to note that there are two transitions observed for chemiluminescence intensity of rubrenesulfonate, in the presence of polyvinylpyrrolidone, with addition of surfactant. The first transition occurs at a SDeS concentration,  $X_1$ , below the cmc ( $X_0$ ) of the surfactant in polymer free solution. The second transition occurs at a SDeS concentration,  $X_2$ , greater than  $X_0$ . The values for  $X_0$ ,  $X_1$ , and  $X_2$  are  $8.7 \times 10^{-3} \text{M}$ ,  $4.3 \times 10^{-3} \text{M}$  and  $2.5 \times 10^{-2} \text{M}$ , respectively.<sup>16</sup>

The effect of chain length of the sodium alkyl sulfates, on the fluorescence and peroxyoxalate chemiluminescence of rubrenesulfonate in the presence of PVP was examined. In contrast with the chemiluminescence enhancements, the fluorescence yield of rubrenesulfonate decreased when all of the sodium alkylsulfate were added to the solution. In the presence of the polymer, only the  $C_{12}$  surfactant, sodium dodecylsulfate approached the effectiveness of SDeS in increasing the peroxyoxalate chemiluminescence. However, the shorter chain surfactants,  $C_6$ ,  $C_7$  and  $C_8$  did exert a modest improvement in chemical light output (Figure 8).

Figure 8. Aqueous Peroxyoxalate Chemiluminescence of Rubrenesulfonate in the Presence of PVP and Sodium Alkylsulfates. The chemiluminescence emission, monitored at 575 nm, was initiated by the addition of water. The PVP and sodium alkylsulfate concentrations were all 1% w/v.

# EFFECT OF CHAIN LENGTH ON POLYMERIC CHEMILUMINESCENCE ENHANCEMENT



## DISCUSSION

The working hypothesis for peroxyoxalate chemiluminescence (equations 1-3) suggests at least three areas where aqueous organized assemblies may influence reaction pathways. The most apparent influence of these assemblies would be on the fluorescence quantum yield,  $\phi_f$ , a significant component to the total chemiluminescence efficiency (equation 4). The efficiency of chemical excitation of the fluorescer,  $\phi_r$ , should be influenced by the heterogeneous environment in which the peroxyoxalate chemiluminescence reaction occurs. For example, the reaction of the energy-releasing intermediate to generate the excited state of the fluorescer,  $Flr^*$ , and carbon dioxide (equation 2) probably requires some interaction or association between the fluorescer and the dioxetanedione.<sup>6,17</sup> In addition, one should not rule out an effect of organized assemblies on the efficiency,  $\phi_{eri}$ , of the bimolecular reaction to generate the energy releasing intermediate (equation 1).

The observation of dramatic surfactant and polymer effects on both fluorescence and chemiluminescence is rather unique. Although, considerable insight is available from the literature on the influence of organized assemblies on fluorescence emission,<sup>18</sup> one can only speculate as to the exact causes for the dramatic chemiluminescence enhancements described within. This is especially true when the emission results from peroxyoxalate chemiluminescence, a reaction whose mechanistic

pathways are not even delineated in homogeneous environments. Thus, the discussion will focus on the conditions required to observe the enhancements in peroxyoxalate chemiluminescence and a comparison with the corresponding influence on fluorescence emission.

Fluorescence Effects - Rubrenesulfonate appears to behave in a manner similar to the parent hydrocarbon. Rubrene has a fluorescence quantum yield of near unity, in nonpolar media, but a reduced emission intensity is observed in polar environments.<sup>19</sup> The fluorescence intensity of rubrenesulfonate is sharply influenced by the hydrophobicity of the solvent. In the alcohol series methanol, ethanol, and 1-propanol, the fluorescence intensity of rubrenesulfonate increases in magnitude as the solvent polarity decreases. Since  $\phi_f$  is impaired with exposure to water, the fluorescence intensity of aqueous solubilized rubrenesulfonate should reflect the average microenvironment experienced by the fluorescer in the organized assemblies.

In the presence of both Deceresol NI and PVP, the fluorescence intensity of aqueous solubilized rubrenesulfonate increases. The observed two-fold fluorescence enhancement, in both cases, suggests that the fluorescer, in general, experiences a hydrophobic environment. The plot of rubrenesulfonate fluorescence intensity against Deceresol NI concentration ([Dec]), is suggestive of a micellar effect on emission



enhancement (Figure 2). The plot reveals that for [Dec] greater than  $10^{-5}M$ , a gradual increase in fluorescence intensity is observed with a maximal increase at [Dec]  $10^{-3}M$ . The broad transition observed in this plot is not unusual for measurements of surface property changes for these type of nonionic surfactants.<sup>12</sup> The profile of this plot certainly suggests that the hydrophobic environment experienced by the fluorescer is a result of sequestering of the fluorescer within a nonionic micelle.

There is considerable evidence in the literature that organicanions bind to aqueous solubilized polyvinylpyrrolidone.<sup>14,15</sup> It would appear that the fluorescence enhancements observed with addition of PVP to aqueous solution of rubrenesulfonate is a manifestation of this fluorescer-polymer association. The resultant microenvironment experienced by the associated rubrenesulfonate is hydrophobic and probably arises from exposure of the rubrene nucleus to the hydrophobic backbone of the polymer chain. The net hydrophobic microenvironment experienced by the fluorescer, in its association with PVP, appears to be similar to the hydrophobic environment that rubrenesulfonate is exposed to when sequestered within a Deceresol NI micelle.

The absence of any influence on the fluorescence efficiency of rubrenesulfonate, by sodium alkylsulfate surfactants, suggests that either the fluorescer is not associated with the resultant

micelles or is localized within the polar palisade layer of the micelle. It might be that the latter is more appropriate because of the ready association of rubrenesulfonate with Deceresol NI. In any case, the net microenvironment experienced by the fluorescer is substantially the same as when rubrenesulfonate is solubilized in water.

### Chemiluminescence Effects

A. Enhancements Due to Micelles - In the previous work, Mohan et.al. reported that while the nonionic surfactant Deceresol NI gave the most dramatic enhancements, cationic surfactants (e.g.; hexadecyltrimethylammonium halides (HDTCl)) provided no positive impact on peroxyoxalate chemiluminescence yields.<sup>10</sup> Likewise, the anionic surfactant SDS was reported to result in a peroxyoxalate chemiluminescence output one-half as great as that obtained with Deceresol NI, with their formulation.<sup>10</sup>

In the absence of polymers, the chemiluminescence enhancements observed with addition of surfactants must be related to the aggregation of the surfactants to form micelles. This is apparent from the dependence of chemical light yields as a function of increasing surfactant concentration (Figure 3 and 4). In general, a dramatic increase in chemiluminescence yields was observed only when the surfactant concentration was greater than the "expected" critical micelle concentration; i.e. cmc.

Since rubrenesulfonate fluoresces with increased efficiency in a hydrophobic environment, one might anticipate that its peroxyoxalate chemiluminescence would be maximized when the fluorecser is buried within the interior of a micelle, where water penetration is minimal. However, as stated earlier, it is likely that the energy releasing intermediate, generated from METQ (equation 1), must interact with rubrenesulfonate to generate carbon dioxide, and chemiexcite the fluorecser (equation 2). Although the net environment experienced by the dioxetanedione cannot be determined from this study, its low molecular weight and high oxygen content suggest that it would not be inhibited from dissolving in a hydrophilic region of these aqueous assemblies. Hence, a fluorecser buried deep within a micelle may not interact as efficiently with the energy releasing intermediate as one somewhat exposed to the aqueous phase. This concept could be tested by, for example, by separating the rubrene chromophore from the sulphonate moiety by  $\{CH_2\}_n$  groups of varying length. Under these conditions, one might expect that a rubrene fluorecser with  $n=12$  would have a maximal fluorescence efficiency but minimal peroxyoxalate chemiluminescence.

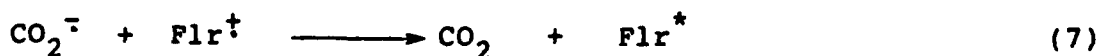
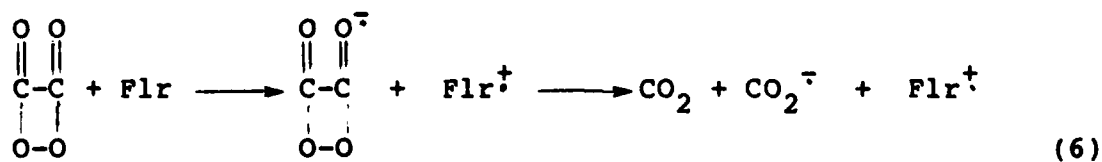
In this study, the rubrenesulfonate utilized corresponded to  $n=0$  and, hence, one would expect the fluorecser to be localized in the polar palisade layer of the micelle. In return for a less than optimal fluorescence efficiency (because of exposure to water), the accessibility to the energy releasing intermediate

allows for peroxyoxalate chemiluminescence. This strategy may be operable with rubrenesulfonate solubilized within Deceresol NI micelles. Nonionic surfactants typically generate micelles that experience considerably more water penetration than corresponding ionic micelles of similar size and surfactant aggregation numbers. Although the fluorescence of rubrenesulfonate solubilized in the Deceresol NI micelle is not maximized, the accessibility of the fluorescer to the water layer allows for its interaction with the dioxetanedione. The net effect is a micellar enhancement of peroxyoxalate chemiluminescence, since both the  $\phi_f$  and  $\phi_{eri} \times \phi_r$  terms, from equation 4, are probably increased with the presence of Deceresol micelles.

A contrast between fluorescence and peroxyoxalate chemiluminescence is most striking in the presence of SDeS micelles. The lack of fluorescence enhancement with micellization is attributed to the net hydrophilic environment experienced by the fluorescer rubrenesulfonate when solubilized in the polar palisade layer of the SDeS micelles. The increased chemiluminescence, however, is consistent with the hypothesis that the enhancement requires accessibility of the fluorescer to the dioxetanedione. The enhanced chemiluminescence yield, in the presence of SDeS micelles, results primarily from the  $\phi_{eri} \times \phi_r$  term (equation 4) since  $\phi_f$  is unchanged in that sodium alkylsulfate formulation.

A similar contrast between fluorescence and chemiluminescence enhancements is observed with HDTCl micelles. The fluorescence intensity of rubrenesulfonate solubilized within HDTCl micelle is even greater than the enhancement observed with Deceresol NI micelles. Nevertheless, there is no peroxyoxalate chemiluminescence enhancement for rubrenesulfonate solubilized in the presence of the cationic surfactant. Hence, although the term  $\phi_f$  (equation 4) is increased in this formulation, the term  $\phi_{eri} \times \phi_r$  must be remarkably decreased in the presence of this quarternary ammonium surfactant.

A hypothesis to account for the difference between sulfate and quarternary ammonium surfactants provides some specifics on where micelles play a role in peroxyoxalate chemiluminescence. Within the context of a chemically initiated electron exchange luminescence (CIEEL) mechanism,<sup>20</sup> the chemiexcitation step (equation 2) may be broken down to an electron exchange and cleavage step (equation 5) and a radical ion pair recombination step (equation 6).



In the presence of cationic ammonium surfactants, the radical anion,  $\text{CO}_2^{\cdot-}$ , may undergo an electron exchange with the head group of the surfactant, the electron acceptor thereby quenching the chemiexcitation.<sup>21</sup> In the presence of sulfate surfactants, an analogous quenching process (where the head group of the surfactant is the electron donor and the fluorescer radical cation,  $\text{Flr}^{\cdot+}$ , is the electron acceptor) is probably not operable. This proposed quenching in the chemiexcitation step, by quaternary ammonium surfactants, may reveal why water-soluble cationic fluorescers, with ammonium solubilizing groups, work poorly in aqueous peroxyoxalate chemiluminescence.<sup>10</sup>

The chemiluminescence enhancements observed with Deceresol NI and SDeS may result from micellar influence on the radical ion pair recombination step (equation 7) in the chemiexcitation. This hypothesis is based on literature precedent of the influence of micelles on the cage reactions of radical pairs and radical ion pairs that lead to coupling products and exciplex emission, respectively.<sup>18a</sup>

B. Enhancements Due to Micelle Polymer Aggregates - Using a variety of probes the interaction of sodium dodecylsulfate with polyvinylpyrrolidone was shown to provide three distinct regions. When SDS is added to an aqueous solution (< 1%) of PVP, there is no association between the surfactant and polymer until a concentration for SDS of  $X_1$ , is reached. Typically  $X_1$ , is a

[SDS] lower than the cmc for that surfactant. Above  $X_1$ , the surfactant begins to associate with the polymer until a surfactant concentration, [SDS], of  $X_2$  is reached. The three regions are thought to reflect the following physical picture: region I, for which [SDS] ranges for 0 to  $X_1$ , there is essentially no surfactant/polymer interactions; region II, for which [SDS] ranges from  $X_1$  to  $X_2$ , clusters of SDS molecules (termed premicelles) associate with the polymer; region III, free micelles of SDS form and exist in equilibrium with micelles of SDS bound to the polymer.<sup>15</sup>

This description of the SDS/PVP interaction was recently corroborated using pyrene as a fluorescence probe.<sup>16</sup> The profiles generated by that fluorescent technique are very similar to that using peroxyoxalate chemiluminescence, (Figure 4). We similarly see, using 1% PVP (mw. 40,000) and SDeS, three regions that suggest the peroxyoxalate chemiluminescence is strongly influenced by the polymer/surfactant interactions described above. Initially, the chemical light output is unchanged with addition of surfactant. At an  $X_1$  value of  $3 \times 10^{-3} M$  [SDeS], the sudden chemical light enhancement suggests that the premicelle/PVP aggregate play a substantial role in influencing the peroxyoxalate chemiluminescence reactions. After leveling off, a second sudden chemical light enhancement is observed for [SDeS],  $X_2$ , of  $2.5 \times 10^{-2} M$ . It is interesting to note that  $X_1$ , is less than, and  $X_2$  is greater than the cmc of SDeS as measured for the identical formulation by peroxyoxalate chemiluminescence.

This observation further supports the surfactant, SDeS, is interacting with PVP in the previously described fashion.

It is especially important to note that the chemiluminescence output in the SDeS/PVP formulation (with [SDeS] of  $4 \times 10^{-2}M$ ) is substantially greater than that output, with identical [SDeS], in the absence of polymer (Figure 9). As [SDeS] is further increased, one would expect the concentration of free SDeS micelle to increase at the expense of SDeS/PVP micelle/polymer aggregates. Hence, the total peroxyoxalate chemiluminescence yield for rubrenesulfonate, in the presence of PVP, would decrease as the [SDeS]  $> 4 \times 10^{-2}M$  was utilized. In fact some dropoff in yield at these higher concentrations has been observed, but have not been extensively explored in this study.

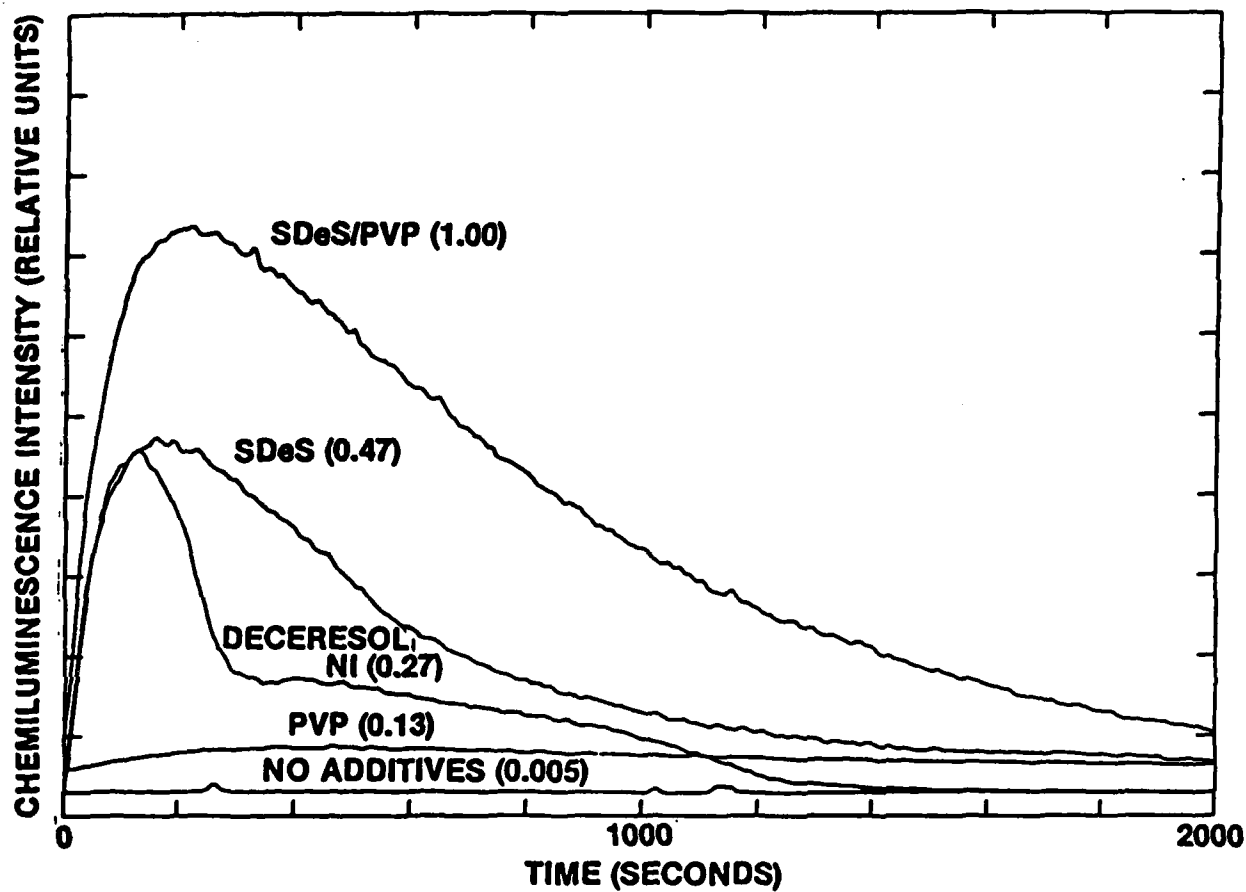
The concepts discussed in micellar enhancements of peroxyoxalate chemiluminescence probably play a role in the presence of these polymer-surfactant aggregates. The net increase in chemiluminescence results from an increase in both  $\phi_{eri} \times \phi_r$  and the  $\phi_f$  terms (equation 4).

C. Enhancement Due to Polymer - Fluorescer Aggregates - The chemiluminescence enhancements observed with the surfactants, are assignable to the phenomenon of micellizations or, in the presence of PVP, well-defined surfactant polymer interaction.



Figure 9. Aqueous Peroxyoxalate Chemiluminescence of Rubrenesulfonate with Various Additives. The chemiluminescence emission, monitored at 575 nm, was initiated by the addition of water. The additives (concentrations) are: PVP (1% w/v); Deceresol NI ( $2 \times 10^{-3}$  M), SDeS ( $3 \times 10^{-2}$  M); and SDeS/PVP ( $3 \times 10^{-2}$  M/1% w/v). The numbers in parantheses are the quantum yields for chemiluminescence relative to the best system.

**MAXIMUM CHEMILUMINESCENCE INTENSITY  
FROM SEVERAL DIFFERENT ADDITIVES**



In addition, the addition of PVP to surfactant-free solution, also resulted in an enhancement of peroxyoxalate chemiluminescence (Figure 7). It is clear, from the fluorescence studies (Figure 6), that in aqueous solutions, with PVP, rubrenesulfonate sees a relatively hydrophobic environment, consistent with the strong association of organic anions to the polymer. The chemiluminescence enhancements are greater in magnitude than the corresponding fluorescence enhancements. In both cases, these enhancements demonstrate the dramatic effects that can be obtained by PVP aggregation with hydrophobic organic anions.

#### Relative Chemiluminescence Yields

The best previously reported aqueous-based peroxyoxalate system, reported by Mohan, et.al., utilized Deceresol NI as an additive to their formulation.<sup>10</sup> From the experiments reported herein, our best aqueous peroxyoxalate formulation uses sodium decylsulfate ( $3 \times 10^{-2}M$ ) and polyvinylpyrrolidone (1% (W/V)). In fact, the chemiluminescence yield for SDeS/PVP is 270% greater than that obtained with Deceresol NI as a direct replacement for the polymer surfactant system (Figure 9).

It is interesting to note that the formulation using the sodium alkylsulfate, SDeS, results in a chemiluminescence yield about 1 1/2 times as great as that obtained with Deceresol NI. The surfactant-free PVP formulation provided the lowest

enhancements, although still substantially improved compared with a surfactant and polymer-free formulation. The relative quantum yields for peroxyoxalate chemiluminescence of rubrenesulfonate (Figure 9) demonstrates these dramatic improvements.

## CONCLUSION

The dramatic enhancements we have observed for aqueous-based peroxyoxalate chemiluminescence of rubrenesulfonate represents a major step forward in improving the practical efficiency of these systems. It is particularly interesting that the enhancements are as a result of well defined surfactant properties. Since the chemiluminescence mechanism is multistep and rather complex, it is not obvious that those properties of organized assemblies would influence the relative efficiencies.

The interaction between surfactants and polymers have played an important role in obtaining the 270% improvement in peroxyoxalate chemiluminescence, in comparison with the previously reported formulation using Deceresol NI.<sup>10,13</sup> It is clear that the enhancement observed using both SDeS and PVP result from a synergistic effect between surfactants and polymers. This synergism allows for the formulation, using both SDeS and PVP, to result in the highest aqueous peroxyoxalate chemiluminescence output to date. The extent of the improvement in chemiluminescence by this surfactant/polymer synergism is quite dramatic: 110% in comparison with the polymer-free SDeS formulation and 670% in comparison with the surfactant-free PVP formulation.

The discovery of the synergistic influence of surfactants with water-soluble polymers on aqueous peroxyoxalate chemiluminescence should not be considered as serendipitous. The interaction of sodium alkylsulfate surfactants with aqueous solubilized PVP has been noted before.<sup>15,16</sup> The peroxyoxalate chemiluminescence of rubrenesulfonate appears to be strongly influenced by these surfactant polymer interactions as demonstrated within. It would appear that this surfactant/polymer synergism will play a major role in enhancing aqueous peroxyoxalate chemiluminescence in comparison with the enhancements observed with formulations using only surfactants<sup>22</sup> or only water-soluble polymers.

Despite the progress made in this work, the understanding of the influence of surfactants and polymers aggregation on aqueous peroxyoxalate chemiluminescence is still incomplete. The exact causes for the observed enhancements remain elusive, although they are obviously related to the heterogeneous environments generated by these aqueous aggregates. Further work will certainly be required to explore the scope of the enhancement we report and to provide for a detail accounting of the reaction enhancements. This is especially true with respect to the impressive results obtained with SDeS-PVP aggregates. The effects of these aggregates on aqueous chemical reactions is only recently being reported. We hope our work will inspire additional efforts in this area.

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